



Cross-linked poly(vinyl alcohol)/poly (diallyldimethylammonium chloride) as anion-exchange membrane for fuel cell applications

Jing Zhang^a, Jinli Qiao^{a,*}, Gaopeng Jiang^{a,2}, Lingling Liu^{a,1}, Yuyu Liu^{b,*}

^a College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, China

^b Lab of Urban and Regional Environmental Systems, Graduate School of Environmental Studies, Tohoku University, Aramaki, Aza Aoba 6-6-11, Aoba-ku, Sendai 980-8579, Japan

HIGHLIGHTS

- PVA/PDDA hydroxyl anion conducting membranes have been developed.
- The concentration and mobility of charge carries of the membranes are measured.
- The membrane displays the high OH[−] conductivity of 0.025 S cm^{−1} at 25 °C.
- The membrane exhibits alkaline stability in 8 M KOH at 80 °C for 360 h.
- A H₂/O₂ fuel cell test at 25 °C yields beginning peak power density of 35.1 mW cm^{−2}.

ARTICLE INFO

Article history:

Received 6 January 2013

Received in revised form

26 March 2013

Accepted 27 March 2013

Available online 10 April 2013

Keywords:

Alkaline anion-exchange membrane

Cross-linking

Hydroxide conductivity

Stability

Membrane electrode assembly

ABSTRACT

The novel, low-cost anion-exchange membranes (abbreviated as PVA/PDDA-OH[−]), made from poly(vinyl alcohol) and poly(diallyldimethylammonium chloride) blends, are successfully synthesized by a combined thermal and chemical cross-linking technique. The hydroxide (OH[−]) conductivity, water uptake, ion exchange capacity (IEC), thermal stability, oxidative stability and alkaline stability of PVA/PDDA-OH[−] membranes are measured to evaluate their applicability in alkaline fuel cells. The effects of cross-linking procedure, cross-linking time and membrane composition on OH[−] conductivity are studied using AC impedance technique. It is found that by cross-linking modifications, the membranes exhibit excellent thermal stability with onset degradation temperature high above 170 °C, a relatively high oxidative stability at 60 °C, and a strong alkaline stability in 8 M KOH at 80 °C. High OH[−] conductivity of 0.025 S cm^{−1} is achieved at 25 °C and reaches up to 0.037 S cm^{−1} at 80 °C. For exploring the conducting mechanisms, the concentration and mobility of charge carries of the membranes are also measured. The H₂/O₂ fuel cell tests with PVA/PDDA-OH[−] membranes yield the peak power density of 11.5 mW cm^{−2} and greatly increase to 35.1 mW cm^{−2} depending on PVA/PDDA mass ratio, on a low metal loading on both the anode and the cathode of 0.5 mg (Pt) cm^{−2} at ambient temperature.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are energy conversion devices that produce electricity by electrochemical reaction between fuel such as hydrogen and oxidant such as oxygen. Because of zero/low emissions when they are used as portable, automobile and stationary powers, the PEMFC are

expected to be the most promising environmentally-friendly power sources [1]. Among which most attention has been focused on the proton-exchange membrane (PEM) fuel cells since they show the excellent chemical, mechanical, and thermal stability as well as high ionic conductivity. However, several challenges should be overcome before the large commercial applications of this technology, such as the high cost of system components including Pt-based electrocatalysts and perfluorosulphonic acid (PFSA) membranes. To solve these problems, recently, great interests have been evoked on alkaline membrane fuel cells (AMFCs). These cells use the alkaline anion-exchange membranes (AAEMs) to displace the proton-exchange membranes (PEMs) with OH[−] anions instead of H⁺ cations [2], thus can get faster electrokinetics, lower fuel

* Corresponding authors. Tel.: +86 21 67792379; fax: +86 21 67792159.

E-mail addresses: qiaojl@dhu.edu.cn, qiaojinli@hotmail.com (J. Qiao), liu@mail.kankyo.tohoku.ac.jp (Y. Liu).

¹ Present address: Pearl Hydrogen Technology Co., Ltd, Shanghai 201803, China.

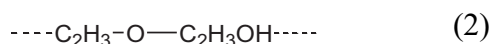
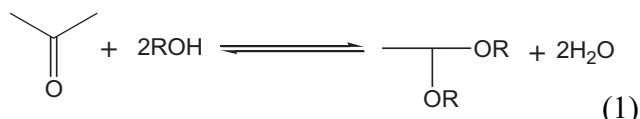
² Present address: University of Waterloo, Ontario, N2L 3G1 Canada.

crossover, reduced CO poisoning, and use of non-precious metal catalysts [3].

In the past several years, some new AAEMs have been successfully explored on the basis of quaternized polymers such as polysiloxane (PSO) [4], poly(oxyethylene) methacrylate (POEM) [5], polysulphane (PS) [6], poly(arylene ether sulfone) (PAES) [7], polyethersulfone cardo (PES-C) [8], poly(phthalazinon ether sulfone ketone) (PPESK) [9], poly(ether imide) (PEI) [10] and radiation-grafted PVDF and FEP [11]. However, these polymers were generally of high price and their quaternization is complex process, which is even toxic and carcinogenic [12]. Moreover, these membranes were unstable in alkaline media especially at temperatures above 60 °C and at high KOH concentrations (above 1 M) [13–17]. Therefore, developing alkaline membranes with desirable properties is still an urgent issue [18,19].

In this paper, we proposed a new type of alkaline membrane based on poly(vinyl alcohol) (PVA) and poly(diallyldimethylammonium chloride) (PDDA) blends. PVA is a polyhydroxy polymer which is very commonly used in practical applications because of its easy preparation and biodegradability [20]. In the meantime, PVA has film-forming capacity, hydrophilic properties, and a high density of reactive chemical functions that are favorable for cross-linking by irradiation, chemical, or thermal treatments [21]. PDDA, a water soluble quaternized copolymer, thus can offer conductive anions (OH^-) as charge carriers. In particular, in our most recent work, the cyclic quaternary ammonium structure with the modification of high dense of cross-linkages of PVA matrix are found to be alkaline tolerance even at some high concentrations of KOH solution, yet the lower OH^- conductivity is still remained to solve [22].

Normally, PVA can be thermally cross-linked by heat treatment, thus the density of membrane prepared can be increased by annealing (thermal treatment) under heat for a certain period of time. Annealing can also help increase the thermal stability of the membrane. In addition, the chemical cross-linking of the hydroxyl groups of PVA with acetal ring is easily formed by applying glutaraldehyde as cross-linker [22]. The chemical and thermal cross-linking reactions can be described as follows [23]:



Based on the above conceptions, in this work, we try to fabricate PVA/PDDA (a cyclic structure in PDDA) polymer blend by a combined thermal and chemical cross-linking technique. Furthermore, the simplicity of the blending technique allows the membrane to be cost-effective, provides the potential for combining the attractive features of each blend component while at the same time reducing their deficient characteristics. The properties of the membranes synthesized such as hydroxide (OH^-) conductivity, water uptake, the ion-exchange capacity (IEC), stability and membrane structure were all characterized using AC impedance technique, FT-IR spectra and TG analysis. The concentration and mobility of charge carriers of the membranes were also measured for exploring the conducting mechanisms with respect to those of commercial available membrane. We will demonstrate that, compared to the state of the art in anion exchange membranes as proposed above [4–17], the membranes developed in this work are cost-effective, easier preparation and also perform high OH^-

conductivity along with the perfect alkaline stability and promising power density.

2. Experimental

2.1. Material and membrane preparation

The membrane was prepared by a simple solution-casting method. A stock PVA (99% hydrolyzed, average molecular weight: $M_w = 86,000\text{--}89,000$, Aldrich) aqueous solution was prepared by dissolving PVA (50 g) in distilled water (500 ml) and then heating at 90 °C with continuous stirring until a transparent solution was obtained. Appropriate amounts of PDDA (20% water solution, average molecular weight: $M_w = 400,000\text{--}500,000$, Aldrich) was then mixed with the above PVA solution in selected blend ratios: PVA/PDDA being 1:0, 1:0.125, 1:0.25, 1:0.5, 1:0.75 and 1:1 by mass. The resulting mixture took on a homogeneous and transparent appearance, then the resulting solutions were poured into plastic Petri dishes, and water was evaporated under ambient conditions. When visually dry, the membrane was peeled from the plastic substrate with a thickness of about 60–80 μm .

2.2. Thermal and chemical cross-linking of PVA/PDDA membranes

To investigate the thermal and chemical cross-linking effect on membrane performances, cross-linking processes were proceeded by the four following ways: (i) the chemical cross-linking time was ranged from 15 min to 7 h without annealing the membrane; (ii) the chemical cross-linking time was ranged from 15 min to 7 h while kept the annealing temperature of the membrane at 130 °C for 1 h. The above two processes were used for study of chemical cross-linking effect. (iii) the annealing time for the membranes was ranged from 15 min to 6 h at 130 °C, while kept the chemical cross-linking time for 1 h; (iv) the annealing temperature was ranged from 110 to 150 °C for 1 h, while kept the chemical cross-linking time for 1 h. The above two processes were used for the study of thermal cross-linking effect. Finally, the most acceptable procedure of thermal and chemical cross-linking was chosen. As a typical candidate, the samples of square pieces of membranes (ca. $1.5 \times 2\text{ cm}$) were annealed at 140 °C for an hour for thermal cross-linking, then were soaked in a reaction solution containing 10 mass% glutaraldehyde (GA: 25 wt% solution in water: SCRC) in acetone for chemical cross-linking with a small amount of hydrochloric acid (0.2%) as catalyst for 1 h.

2.3. Preparation of alkaline PVA/PDDA- OH^- membranes

Fig. 1 schematically illustrates the preparation of thermally and chemically cross-linked PVA/PDDA membranes. The membranes were rendered conducting by immersion of PVA/PDDA membranes in 2 M KOH and equilibrated for 24 h to convert it from Cl^- form into OH^- form. Thus, the PVA/PDDA-based AAEMs are abbreviated as PVA/PDDA- OH^- , then the membranes were taken out and rinsed repeatedly with deionized (D.I.) water to remove the absorbed KOH on membrane surfaces for final conductivity measurements. A model of the inner structure of PVA/PDDA- OH^- was given in Fig. 2.

2.4. OH^- conductivity measurement

The OH^- conductivity of the formed membrane was measured by an AC impedance technique using an electrochemical impedance analyzer (CHI760), where the AC frequency was scanned from 100 kHz to 0.1 Hz at a voltage amplitude of 100 mV. Fully hydrated membranes were sandwiched in a Teflon conductivity cell equipped with Pt foil contacts on which Pt black was plated [24,25]. The membranes were in contact with water throughout the

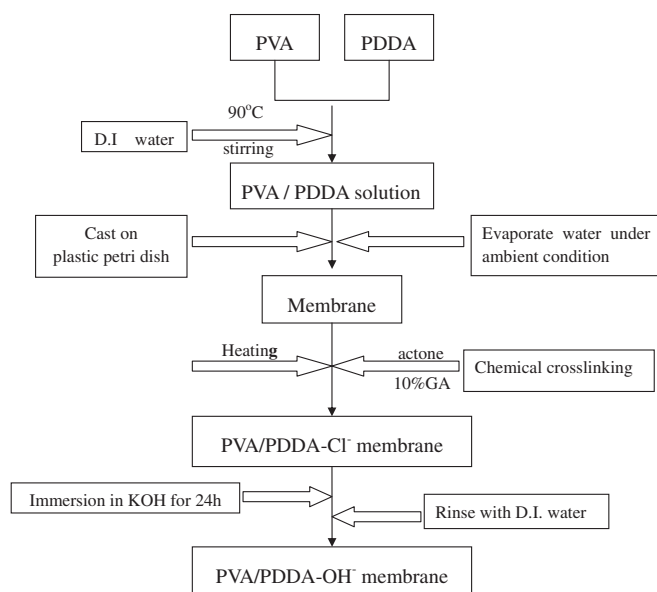


Fig. 1. Schematic diagram for the preparation of PVA/PDDA-OH[−] alkaline membranes by blending and cross-linking.

measurement. The impedance was measured by placing the cell in a temperature range of 25–80 °C. Then OH[−] conductivity (S cm^{−1}) was calculated according to the following equation:

$$\sigma = l/(RTW) \quad (3)$$

where l is the length of the membrane between two potential sensing platinum wires, R is the membrane resistance, and W and T are the width and thickness of the membrane, respectively.

As a reference, anion-exchange membrane, Tokuyama A901, was also measured under the same measuring conditions. Here, Tokuyama A901 is a major type of commercially available membrane, which exhibited high OH[−] conductivity of 11.4 mS cm^{−1}, ion exchange capacity of 1.7 mequiv g^{−1}, quite excellent chemical

stability and power density [26], and generally used as a reference when comparing membrane characteristics and fuel cell performances. The details can be referenced [27].

2.5. Ion exchange capacity (IEC) and water uptake

The ion exchange capacity (IEC, mequiv g^{−1}) of the membranes was determined using the classical titration method. The composite membrane was soaked in 100 ml of 2.0 M KOH solution to convert into the OH[−] form. The membrane was washed with D.I. water to remove excess KOH, then equilibrated with 25 ml of 0.1 M HCl solution for 24 h. The IEC value was determined from the reduction in acid measured using back titration. The IEC value is defined as mequiv of quaternary ammonium groups per gram of dried sample.

The swelling of the membrane was evaluated by the water uptake (WU) from the mass change before and after complete dryness of the membrane. A dry membrane was swollen in D.I. water for a day, then the surface water was carefully wiped with a filter paper, and it was immediately weighed. After drying the sample overnight at 60 °C, the water uptake (WU), was calculated using the expression:

$$WU = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \quad (4)$$

where W_{wet} and W_{dry} are the mass of the fully hydrated membrane and of dry membrane, respectively.

2.6. Structure characterization

The molecular structure of PVA/PDDA-OH[−] membranes was characterized by Fourier transform infrared (FTIR) spectroscopy. The infrared spectrometer (Tensor 27, Bucker) equipped with attenuated total reflectance (ATR) instrument was used to obtain the spectrogram with a wavenumber resolution of 4 cm^{−1} in the range from 4000 to 600 cm^{−1}.

The gravimetric analysis (TG) of membranes was carried out with a TG 209 analyzer (Netzsch). Samples of 5 mg loaded into an alumina oxide pan were heated from 25 to 600 °C at a heating rate of 10 °C min^{−1} with 20 ml min^{−1} nitrogen gas flowing as protection.

2.7. MEA fabrication and single-cell performance measurements

The catalyst ink was prepared by mixing 40% Pt/C (Johnson Matthey) with a solution of 5 wt% Nafion (DuPont) and isopropanol, and then sonicated for 4 h to get a homogeneous solution, where the ratio of Pt/C catalyst to Nafion was 3:1. The catalyst ink was sprayed onto the carbon paper (Toray TGP-H-090) to deposit a catalyst layer with a Pt loading of 0.5 mg cm^{−2} for both the anode and the cathode. Then four drops of alkaline ionomer, Tokuyama AS-4, were loaded on the catalyst layers.

The MEA was fabricated by hot-pressing the PVA/PDDA-OH[−] membrane with the catalyst loaded carbon paper at a pressure of 6 MPa at 50 °C for 6 min. The MEA was evaluated in a single fuel cell with an active area of 4 cm² in H₂/O₂ gas using an electronic load. Pure hydrogen and oxygen were supplied to enter the anode and cathode channels at a flow rate of 100 and 70 ml min^{−1}, respectively, through a humidifier maintained at 25 °C under ambient pressure. Polarization curves were obtained using a fuel cell evaluation system (GE/FC1-100). For comparison, a single-cell test was also carried out in which the MEA was fabricated with Tokuyama A901.

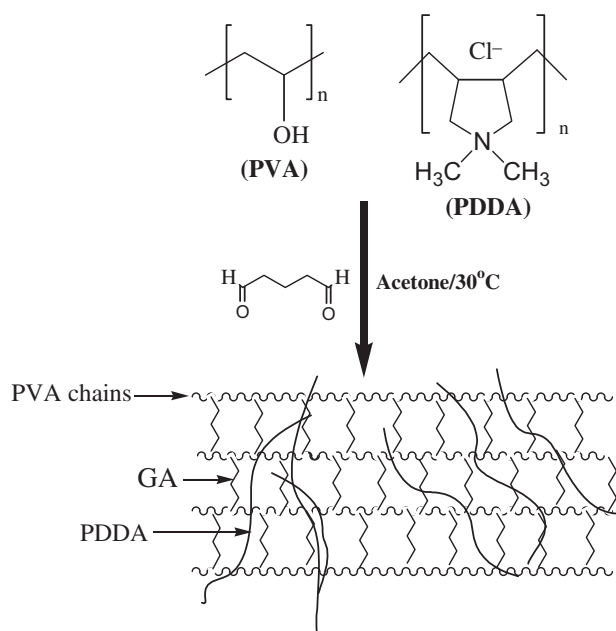


Fig. 2. Structures of PVA, PDDA and cross-linked PVA/PDDA-OH[−] alkaline membranes.

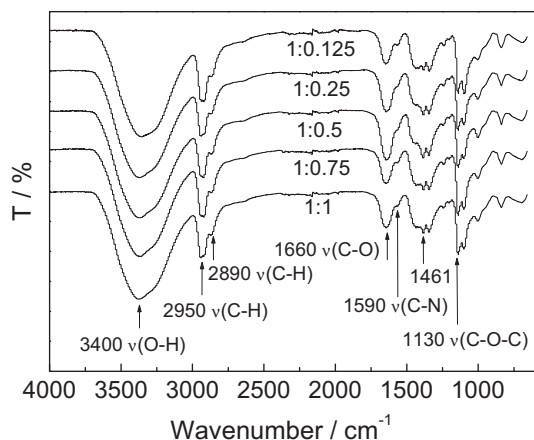


Fig. 3. FTIR spectra of PVA/PDDA-OH[−] alkaline membranes in different content of PDDA.

3. Results and discussion

3.1. FT-IR spectra

Fig. 3 gives the typical FT-IR spectra measured for PVA/PDDA-OH[−] alkaline membranes in different PDDA contents after chemical cross-linking modifications. The spectra display the wavenumber region between 4000 and 400 cm^{−1}, which covers the frequencies of the entire IR vibrations characteristic of interactions between PVA and PDDA-OH[−]. All of the spectra show an intense band between 3100 and 3750 cm^{−1}, which is ascribed to the stretching vibration of −OH groups from PVA or the possibly bound water during the measurement. The peaks at 2950 and 2890 cm^{−1} arise from the

stretching of CH₃−, −CH₂−, and CH− groups. Different from PVA complexed other quaternized polymer systems, here the sharp absorption band at 1718 cm^{−1} (C=O) was not observed due to the ‘free’ −CHO attached to GA [24,25]. However, the presence of cross-linking in the PVA matrix was demonstrated by the appearance of a strong absorption band at 1660 cm^{−1} (C=O), which can be ascribed to the cross-linking reaction between −OH groups of PVA and −CHO groups of GA. The peak at 1130 cm^{−1} corresponding to the vibration of C−O−C also indicates the presence of cross-linking network in PVA matrix. The appearance of a shoulder peak centered at 1590 cm^{−1} is owing to the stretching vibration absorption of C−N of PDDA, indicating that PDDA was successfully incorporated into the PVA matrix. It seems that the spectra show no obvious changes as for different content of PDDA in polymer. However, the following differences are still observed in the spectra features: (i) the peak for the absorption bands at 1590 cm^{−1} became stronger with increasing the content of PDDA; (ii) the characteristic peak related to the ring stretching vibrations at 1467 cm^{−1} in 1:0.125 membrane shifted to 1461 cm^{−1} in 1:1 membrane; (iii) the percent of characteristic absorbance of the OH mode at 3400 cm^{−1} increased with PDDA content and slightly shifted from 3390 cm^{−1} in 1:0.125 membrane to 3400 cm^{−1} in 1:1 membrane. All above suggests some hydrogen-bonding interactions of OH or weak molecular interactions between PDDA-OH[−] and −OH groups of PVA [28].

3.2. Ionic conductivity and water uptake

3.2.1. Effect of cross-linking time and cross-linking process

In order to explore the most suitable thermal and chemical cross-linking procedures, the ionic conductivity (σ_{Cl^-}) and water uptake (WU) of PVA/PDDA membranes without KOH ion-exchange have been measured. At this situation, the conductivity of the membrane is due to Cl[−], which is lower than the OH[−] conductivity.

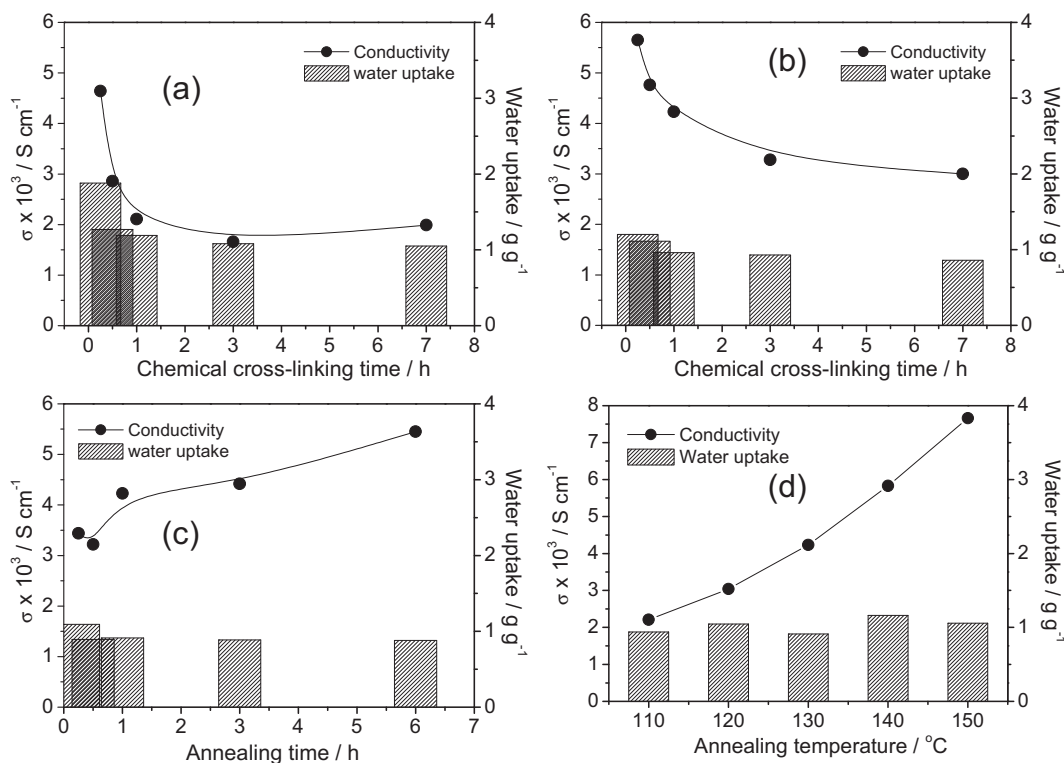


Fig. 4. Cl[−] conductivity and WU of PVA/PDDA membranes as a function of (a) chemical cross-linking time, (b) chemical cross-linking time while kept the annealing temperature at 130 °C for 1 h, (c) annealing time while kept the annealing temperature at 130 °C and chemical cross-linking time for 1 h, (d) annealing temperature while kept the annealing time and chemical cross-linking time for 1 h. Polymer composition PVA/PDDA = 1:0.5 by mass.

Fig. 4(a) shows a typical effect of chemical cross-linking time on both the σ_{Cl^-} value and WU of PVA/PDDA membranes with polymer composition of 1:0.5 (by mass) as a typical candidate without annealing of the membrane. It can be seen that at the initial 1 h cross-linking reaction, the WU decreased sharply with chemical cross-linking time, then tended to level off. Similar trends were obtained for σ_{Cl^-} values. With increasing the cross-linking time, the hydrophobic property of the membranes is increased due to the increased cross-linking density in PVA matrix. This makes the polymer structure more rigid and compact, and results in a decrease in the free volume capable of containing water molecules, thus the decrease in σ_{Cl^-} as shown in Fig. 4(a). However, with further increasing the chemical cross-linking time, for example, larger than 1 h, both WU and σ_{Cl^-} values have no obvious changes, indicating the completeness of the chemical cross-linking reaction. Thus, the optimal reaction time for chemical cross-linking was determined as 1 h for all the membrane samples tested. During this stage, the σ_{Cl^-} value reached up to $2.11 \times 10^{-3} \text{ S cm}^{-1}$ along with the high WU around 1.19 g g^{-1} . The presence of water in the membranes is a prerequisite for reaching high ionic conductivity. Water cluster can offer transport channels for anions inside the anion-exchange membrane [22], thus can improve the ionic conductivity. On the other hand, so high water uptake would lead to the extreme swelling of the membrane, which causes a loss of the dimensional stability. Therefore, for further improving the water uptake, pre-heat treatment was applied for PVA/PDDA membranes. Fig. 4(b) gives the typical results after the annealing of the PVA/PDDA membrane at 130°C for 1 h, then for chemical cross-linking modifications. It can be seen that the WU greatly decreased to 0.91 g g^{-1} compared to 1.19 g g^{-1} for pure chemical cross-linking (Fig. 4(a)). This indicates that annealing can induce the thermal cross-linking in the PVA matrix as Equation (2) showed, which can further improve water absorption of the membranes. To our interest, no loss of σ_{Cl^-} was observed during the annealing process. Conversely, the σ_{Cl^-} values increased from $2.11 \times 10^{-3} \text{ S cm}^{-1}$ (for pure 1 h chemical cross-linking) to $4.23 \times 10^{-3} \text{ S cm}^{-1}$ (for 1 h chemical cross-linking plus 1 h annealing). This suggests that the water uptake in the membranes could be improved by pre-heat treatment while still approaching high ionic conductivity by optimizing the conditions, such as annealing temperature and annealing time. Fig. 4(c) shows the change in σ_{Cl^-} and WU with annealing time, while the annealing temperature was kept at 130°C , and the chemical cross-linking time was kept at 1 h. As can be seen, the σ_{Cl^-} values increased with the increasing thermal cross-linking time and reached $5.45 \times 10^{-3} \text{ S cm}^{-1}$, although the water uptake decreased a little. Fig. 4(d) shows the change in σ_{Cl^-} and WU with annealing temperature, while the annealing time and chemical cross-linking time were both kept for 1 h. Similarly, the σ_{Cl^-} values increased greatly with the increasing annealing temperature and, reached $7.66 \times 10^{-3} \text{ S cm}^{-1}$ when the annealing temperature reached 150°C . For obtaining both good mechanical property and high OH^- conductivity of the membranes, in this work, the annealing temperature of 140°C for 1 h was found to be the best condition for thermal cross-linking reaction. Lower ($<130^\circ\text{C}$) or higher ($>150^\circ\text{C}$) than this temperature would lead to higher WU (larger than 105%), brittle and/or curling membranes that are not suitable for the practical usage of a fuel cell.

3.2.2. Effect of ionic-exchange concentration and polymer composition

The PVA/PDDA membranes were rendered conducting by soaking in KOH solution to convert it from Cl^- form into OH^- form. In order to clarify any interaction between the KOH concentration and PVA/PDDA membranes, it was assessed by soaking the membranes in different concentrations of KOH (1.0–10 M) solution at

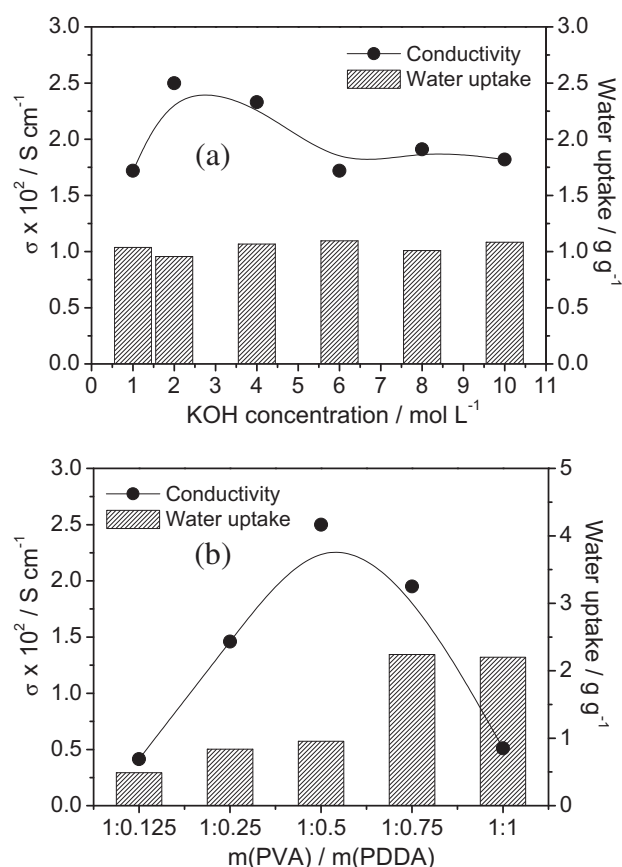


Fig. 5. OH^- conductivity and WU of PVA/PDDA- OH^- alkaline membranes (1:0.5 by mass) as a function of (a) KOH concentration for ion-exchange, (b) PVA/PDDA mass ratio.

room temperature for 24 h. Fig. 5(a) shows the change in OH^- conductivity of PVA/PDDA membranes with different concentrations of KOH solution for ion-exchange. It can be seen that the OH^- conductivity measured by AC impedance spectroscopy reached a maximum value of 0.025 S cm^{-1} for PVA/PDDA membrane after ion-exchange with 2 M KOH aqueous solution, which is much higher than our previously investigated quaternized polymers, such as PAADDA [29] and QHECE [30]. This clearly demonstrated that Cl^- was exchanged by OH^- , although the adsorbed KOH on the surface of the membrane was removed after repeated rinsing with D.I. water. However, the OH^- conductivity decreased with additional KOH concentration in solution for ion-exchange, for example, the σ_{OH^-} value decreased to 0.0183 S cm^{-1} when soaking in 10 M KOH solution. From Fig. 5(a), the WU has no obvious change after ion-exchange in different KOH concentrations in solution, therefore, it is concluded that additional KOH may enter into the polymer chains during the ion-exchange in such a high KOH concentration (10 M) in solution. The decreasing trend in OH^- conductivity with higher KOH concentration is a common phenomenon observed in polymer electrolytes and can be explained in the terms of the weak ionic mobility since the degree of freedom of ion transport is reduced as so much KOH enters into the polymer matrix. Another reason may be the results from decomposition of quaternary ammonium groups from PDDA under such a high KOH concentration in solution. Therefore, the PVA/PDDA- OH^- membranes that we discuss later are all ion-exchanged with 2 M KOH.

Fig. 5(b) shows the OH^- conductivity (σ_{OH^-}) and WU of PVA/PDDA- OH^- membranes as a function of PDDA content, where the PVA/PDDA mass ratio ranged from 1:0.125 to 1:1. Initially, the OH^-

conductivity increased with PDDA content, then reached a plateau (0.025 S cm^{-1}) at a PVA/PDDA polymer composition of 1:0.5 by mass. This can be attributed to an increase in the number of charge carriers in the PVA polymer matrix due to the interpenetrating PDDA domain. Further addition of PDDA to the polymer leads to a decrease in conductivity. The decrease in OH^- conductivity seen when the PVA/PDDA ratio exceeds 1:0.5 by mass may stem from the high water uptake of the membrane due to the increased hydrophilic effect of PDDA. Large sorption of water may due to greater flexibility of the polymer chains or the microstructure of the polymer, which would allow more water to reside between the polymer chains. This, together with the hydrophilic character of PDDA, results in large sorption of water at high PDDA content, which does not simply give improved ionic conductivity but rather a dilution of charge carriers [31].

3.3. The ion exchange capacity (IEC), concentration (C_{OH^-}) and mobility (u_{OH^-}) of charge carries

The concentration (C_{OH^-}) and mobility (u_{OH^-}) of charge carriers are two key factors that influence the conductivity of the membrane. On the one hand, the OH^- conductivity increases with increasing concentration of the charge carriers because of the high charge density of the membranes, on the other hand, the OH^- conductivity increases because of increased mobility of charge carriers in the water phase with increasing water content. Table 1 gives the IEC, concentration and mobility of charge carriers for PVA/PDDA- OH^- alkaline membrane together with those for Tokuyama A901. IEC is known to have the profound effect on membrane conductivity expect for WU. From Table 1, we can see that the IEC increased with the content of PDDA due to the increased quaternary ammonium groups in the membrane, while further addition of PDDA also induced the increasing water uptake due to the increased hydrophilic effect of PDDA. The high water uptake plays an important role in lowering the concentration of charge carriers and lifting the mobility of the charge carriers. In other words, the large increase in the amount of water does not simply make an additional contribution to the mobility of charge carriers but rather a dilution of charge carriers. Therefore, although the PVA/PDDA- OH^- membrane, for example, 1:0.75 membrane has higher IEC than 1:0.25 and 1:0.5 membranes, its excess high water uptake (224%) produces an unfavorable effect on the conductivity. On the other hand, for A901 it showed a higher concentration of charge carriers but a lower mobility in comparison with PVA/PDDA- OH^- alkaline membranes because of the high IEC and very low water uptake of A901. Therefore, the PVA/PDDA- OH^- alkaline membrane would be promising candidate for fuel cells if we could find some way to further suppress its water swelling behavior.

3.4. Temperature dependences of OH^- conductivity

As has been reported, operation of anion-exchange membrane fuel cells at elevated temperature leads to enhanced performances. High temperatures would not only reduce thermodynamic voltage losses due to potential pH gradients through the membrane but

Table 1
Physical parameters of PVA/PDDA- OH^- alkaline membranes and A901.

PVA/PDDA- OH^- (by mass)	σ (S cm^{-1})	IEC (mequiv g^{-1})	WU (g g^{-1})	$C_{\text{OH}^-} \times 10^3$ (mol cm^{-3})	$u_{\text{OH}^-} \times 10^3$ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
1:0.25	0.015	0.77	0.84	0.50	0.30
1:0.5	0.025	0.85	0.96	0.53	0.49
1:0.75	0.020	0.89	2.24	0.45	0.45
A901	0.038	1.80	0.15	1.85	0.21

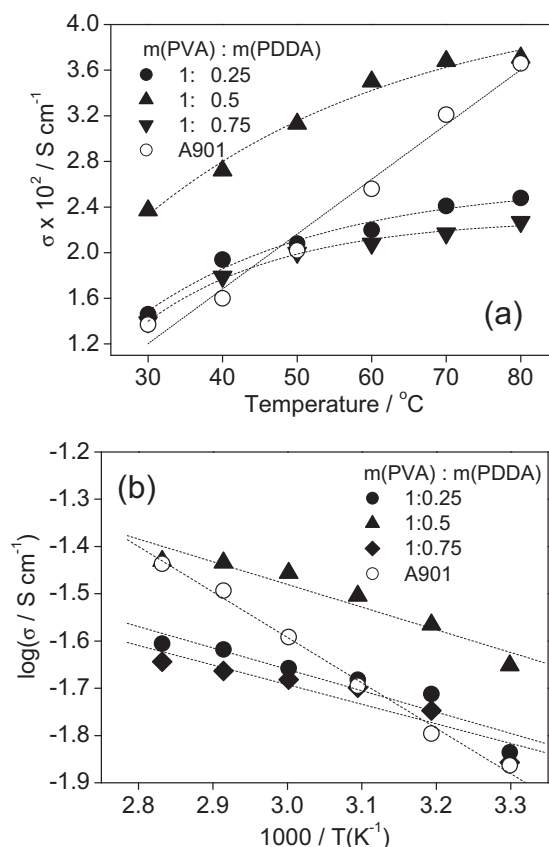


Fig. 6. (a) Temperature dependence of OH^- conductivity, (b) the $\log \sigma$ vs. $1000/T$ plot for PVA/PDDA- OH^- alkaline membranes.

also improve electrokinetics [32]. Fig. 6(a) shows the correlation between OH^- conductivity and temperature for PVA/PDDA- OH^- membranes. For a good comparison, the data for Tokuyama A901 was also presented in Fig. 6(a). All the samples were well hydrated during the test, and eliminated the effect of humidification. It can be seen that the OH^- conductivities were all gradually increased with increasing temperature for PVA/PDDA- OH^- membranes, while the Tokuyama A901 showed a linear increase in OH^- conductivity with temperature. The highest OH^- conductivity of 0.037 S cm^{-1} at 80°C was achieved for PVA/PDDA- OH^- membrane with PVA/PDDA mass ratio being 1:0.5 by mass. This is desirable when uses as alkaline anion-exchange membrane in a fuel cell. From Table 1, the high conductivity is a result of high level of hydration and greater ion mobility. The conductive channels formed by microphase separation create conductive channels in PVA/PDDA- OH^- membranes. The dependence of OH^- conductivity on temperature for low temperature polymer electrolytes is typically taken as Arrhenius type:

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (5)$$

Where σ_0 is a pre-exponential factor, E_a is the apparent activation energy, and T is the thermodynamic temperature in K. The E_a was estimated from the linear regression of $\log(\sigma)$ vs. $1000/T$ as shown in Fig. 6(b), assuming an Arrhenius behavior. Thus, the values of E_a obtained from the Arrhenius plots were 7.94 kJ mol^{-1} (PVA/PDDA = 1:0.25 by mass), 9.20 kJ mol^{-1} (PVA/PDDA = 1:0.5 by mass) and 8.67 kJ mol^{-1} (PVA/PDDA = 1:0.75 by mass) which are close to 10 kJ mol^{-1} , indicating that both the Grotthuss mechanism and Vehicle mechanism existed in the membranes but the former is more dominant [33].

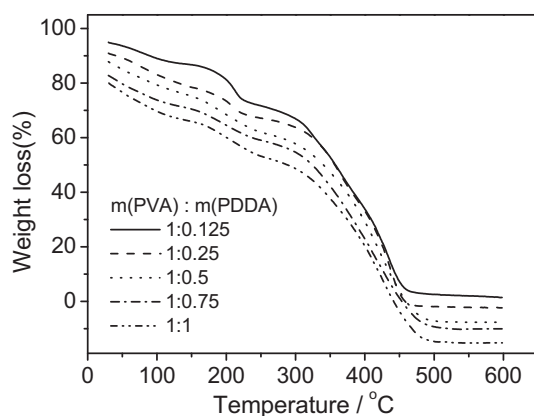


Fig. 7. TG profiles of cross-linked PVA/PDDA-OH[−] alkaline membranes in different content of PDDA.

3.5. Membrane stability

3.5.1. Thermal stability

The thermal stability of the polymer electrolyte is a key metric for fuel cell use. Fig. 7 shows the TG analysis curves of PVA/PDDA-OH[−] membranes with different contents of PDDA. All of the PVA/PDDA-OH[−] membranes displayed three major weight loss stages at around 30–150, 170–280 and 300–450 °C, which belong to the expulsion of water molecules from the polymer matrix or the moisture absorbed from the air, the decomposition of quaternary ammonium groups and the splitting of the PVA main chain as well as the destruction of cross-linking bridge and polymer backbone, respectively. By a further thermal analysis from a derivative of weight loss (the Figure not provided), the onset decomposition temperature of the second weight loss stage started at about 170–190 °C due to the removal of the quaternary ammonium groups. In Fig. 7, we can perceive that increased content of PDDA in the polymer leads to a slight decrease on the thermal onset degradation temperature (from 192.8 °C for PVA/PDDA = 1:0.125 by mass to 171.2 °C for PVA/PDDA = 1:1 by mass). Incorporation of ionic functions from PDDA decreased the thermal stability of the composite membranes due to the nature of polyanion and the less thermal stability of quaternary ammonium groups. However, by changing the content of PDDA from 12.5% to 100%, no obvious mass loss changes were observed and the weight losses were at about 15%. This may be due to the strong thermal and chemical cross-linking networks in PVA matrix (where the PDDA was well trapped), although the active quaternary ammonium groups in the polymer increased with the content of PDDA. This indicates the sufficient thermal stability for general fuel cell operation temperature under 100 °C.

3.5.2. Oxidation stability and alkaline stability

To evaluate the oxidative durability of PVA/PDDA-OH[−] membranes after thermal and chemical cross-linking, time dependent measurements of the weight changes in 3% H₂O₂ solution at an elevated temperature of 60 °C were carried out. In Fig. 8(a), the 1:0.5 membrane was tested as a typical candidate. It was observed that the PVA/PDDA-OH[−] membranes not only showed high OH[−] conductivity, but also exhibited excellent oxidative longevity. As can be seen in Fig. 8(a), an initial sharp decrease in weight percentage (18%) was observed after the membrane samples were soaked in 3% H₂O₂ solution within 24 h. After that, the weight of membrane samples tends to maintain a constant value (about 80 wt%) with no further weight losses again up to 240 h at 60 °C. As a reference, the result for Tokuyama membrane A901 was also

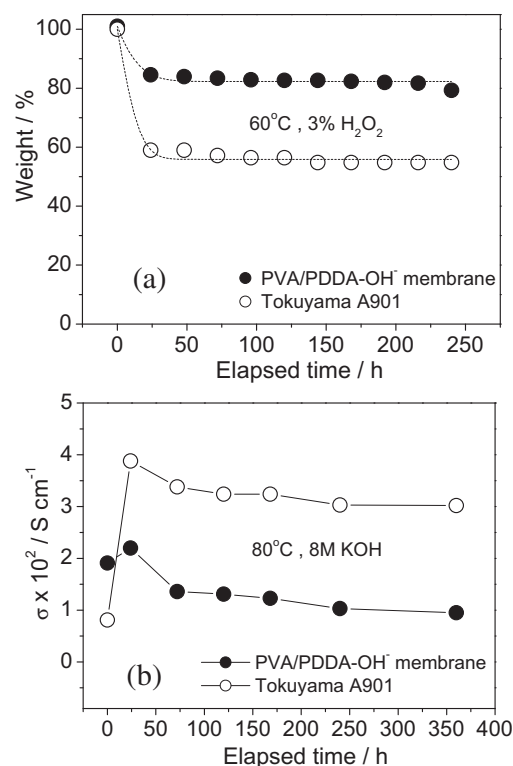


Fig. 8. Time course of (a) weight loss of PVA/PDDA-OH[−] alkaline membranes (1:0.5 by mass) in 3% solution at 60 °C, (b) OH[−] conductivity in 8 M KOH solution at 80 °C. The data for Tokuyama A901 was also presented in the same figure for comparison.

presented under the same measuring conditions. It is interesting to find that PVA/PDDA-OH[−] membrane even shows higher oxidative stability than Tokuyama A901 although the PVA/PDDA-OH[−] membrane is just made of aliphatic skeletons (Fig. 8(a)). The result shows that the PVA/PDDA-OH[−] membrane with thermal and chemical cross-linking technique acquire very promising oxidation stability for application in fuel cells.

The quaternary ammonium groups which are functional groups in the anion-exchange membranes decompose easily by either an E2 (Hofmann degradation) mechanism or an S_N2 substitution reaction [34,35]. Because of this, the chemical stability of alkaline electrolyte membranes is recognized as a key factor that affects their electrochemical applications, especially at high KOH concentrations and at elevated temperatures above 60 °C [14]. In order to investigate the long-term stability of PVA/PDDA-OH[−] membranes, an accelerated aging experiment was carried out, i.e., the membranes (1:0.5 by mass) were soaked in hot 8 M KOH at 80 °C. It was then washed with D.I. water numerous times for complete removal of free KOH on membrane surfaces, then the OH[−] conductivity of the membranes was measured at room temperature. The resultant OH[−] conductivity was recorded at increasing alkali soaking time. Similarly, the result for Tokuyama A901 was also presented for a comparison. As seen in Fig. 8(b), Tokuyama A901 shows very good alkaline stability, where no decrease in OH[−] conductivity was observed during the whole period of testing. The increase in OH[−] conductivity at initial 24 h may be due to more KOH soaked in polymer matrix. For PVA/PDDA-OH[−] membrane, the increase in OH[−] conductivity was also observed during an initial 24 h. Then no obvious decrease in conductivity was observed even after 360 h of soaking and, the OH[−] conductivity was kept at around 0.01 S cm^{−1}. The results suggest that the PVA/PDDA-OH[−] membrane maintains its functional group chemistries under strong alkaline environment. Obviously, the thermal and chemical cross-linking

modification would play an important role in improving the conductivity durability of the membranes. Besides, the excellent alkali stability may derive from the inner structure of the membranes, i.e., the cyclic quaternary ammonium in PDPA although the mechanisms is not very clear at this stage [29]. In short, the PDPA molecules cannot escape from the membrane matrix because of strong entanglement of PDPA entrapped in PVA networks. As a result, the membrane conductivity did not change so much during the whole storage time in the accelerated experiment. All above indicates that the PVA/PDPA- OH^- membranes are quite stable at high temperature even when treated with a KOH concentration up to 8 M at 80 °C.

3.6. Single-cell performances

In Fig. 9, PVA/PDPA- OH^- membranes with three mass ratios (1:0.25, 1:0.5 and 1:0.75) were used to fabricate the MEA, and the real H_2/O_2 single-cell performances were investigated at room temperature. Tokuyama A901 was also used to fabricate MEA for a comparison. The MEAs with 4 cm² activated area and 0.5 mg cm⁻² catalyst loading both on the cathode and anode were prepared with PVA/PDPA- OH^- membranes by hot pressing. The anode stream was hydrogen with flow rate of 100 ml min⁻¹ and the cathode stream was oxygen with flow rate of 70 ml min⁻¹. It can be seen that the cell performances increased significantly with increasing the mass ratio of PVA/PDPA from 1:0.125 to 1:0.5 due to increased OH^- charge carriers, and then decreased with further additional content of PDPA for 1:0.75 membrane, which is in a well agreement with the results of OH^- conductivity of the membranes. The MEAs fabricated with above three PVA/PDPA- OH^- membranes showed the peak power densities around 11.5, 35.1 and 14.8 mW cm⁻², along with the maximum current densities at 73.6, 100 and 64 mA cm⁻², respectively. As for the open circuit voltages (OCVs), the cells with 1:0.5 and 1:0.75 membranes were at 1.0 and 1.1 V, while the OCV for 1:0.25 membrane was at about 0.6 V, which is much lower than that of 1:0.5 and 1:0.75 membranes. Such low OCV was very probably caused by the poor sealing the cells that induced reactant cross-over. Combined with the resistance data in Fig. 6, it can be concluded that cell ohmic resistance is markedly improved with PVA/PDPA- OH^- membrane, where PVA/PDPA = 1:0.5 by mass. It is noted that under the same measuring conditions, the MEA fabricated with Tokuyama A901 showed a peak power density of 37.7 mW cm⁻² and OCV of 1.05 V, which are only slightly higher than those of PVA/PDPA- OH^- membrane (PVA/

PDPA = 1:0.5 by mass). Actually, the cell performances of PVA/PDPA- OH^- membrane are much higher than other polymers with aromatic skeletons, such as GPPG (16 mW cm⁻²) [12], QAPSF (4.1 mW cm⁻²) [36], QPBIs (3.1 mW cm⁻²) [37] and Im-AAEM (30 mW cm⁻²) [38]. Besides the AAEM's properties, the cell behavior is also affected by catalysts, and the MEA fabrication procedures. It should be mentioned that the catalyst ink was prepared by mixing 40% Pt/C (JM) with a solution of 5 wt% Nafion (DuPont) in this work. If the catalyst ink could be made of with quaternary ammonium-type ionomer, we suppose the fuel cell with PVA/PDPA- OH^- membrane could perform better.

4. Conclusions

The novel alkaline anion-exchange membranes, PVA/PDPA- OH^- , were prepared by a combined thermal and chemical cross-linking ways and successfully applied in AAEM fuel cell. High OH^- conductivity of 0.025 S cm⁻¹ at 25 °C was obtained for a polymer composition PVA/PDPA- OH^- being 1:0.5 by mass, and the conductivity increased with temperature up to 80 °C. The strong alkaline stability of the membranes has been achieved in 8 M KOH at 80 °C for 360 h. Meanwhile, the membranes exhibited excellent thermal stability with onset degradation temperature high above 170 °C and, also a relatively high oxidative durability at 60 °C. The above results may be due to the formation of interpenetrating polymer networks of PDPA in the highly cross-linked PVA network by a combined thermal and chemical cross-linking method, which improves not only the OH^- conductivity but also the stability of the membranes. Performance of H_2/O_2 fuel cell with PVA/PDPA- OH^- membrane showed a beginning maximum power density of 35.1 mW cm⁻² and OCV of 1.0 V. These values are very close to commercially available Tokuyama A901 under the same measuring conditions, suggesting that the PVA/PDPA- OH^- membranes could be new prospects for use in alkaline fuel cells.

Acknowledgment

This work is financially supported by National Natural Science Foundation of China (grant no. 21173039); Specialized Research Fund for the Doctoral Program of Higher Education, SRFD (20110075110001) of China; The Opening Foundation of Zhejiang Provincial Top Key Discipline; the Graduate degree thesis Innovation Foundation of Donghua University and the State Environmental Protection Engineering Center for Pollution Treatment and Control in Textile Industry of china. All the financial supports are gratefully acknowledged.

References

- [1] M.A.J. Cropper, S. Geiger, D.M. Jollie, J. Power Sources 131 (2004) 57–61.
- [2] J.R. Varcoe, R.C.T. Slade, E. Lam How Yee, S.D. Poynton, D.J. Driscoll, D.C. Apperley, Chem. Mater. 19 (2007) 2686–2693.
- [3] J.F. Zhou, M. Ünü, I. Anestis-Richard, P.A. Kohl, J. Membr. Sci. 350 (2010) 286–292.
- [4] J.-J. Kang, W.-Y. Li, Y. Lin, X.-P. Li, X.-R. Xiao, S.-B. Fang, Polym. Adv. Technol. 15 (2004) 61–64.
- [5] F. Yi, X. Yang, Y. Li, S. Fang, Polym. Adv. Technol. 10 (1999) 473–475.
- [6] S. Lu, J. Pan, A. Huang, L. Zhuang, J. Lu, Proc. Natl. Acad. Sci. U S A 105 (2008) 20611–20614.
- [7] J. Wang, J. Wang, S. Li, S. Zhang, J. Membr. Sci. 368 (2011) 246–253.
- [8] L. Li, Y. Wang, J. Membr. Sci. 262 (2005) 1–4.
- [9] J. Fang, P.K. Shen, J. Membr. Sci. 285 (2006) 317–322.
- [10] G. Wang, Y. Weng, D. Chu, D. Xie, R. Chen, J. Membr. Sci. 326 (2009) 4–8.
- [11] R. Slade, J. Varcoe, Solid State Ionics 176 (2005) 585–597.
- [12] Y. Zhang, J. Fang, Y. Wu, H. Xu, X. Chi, W. Li, Y. Yang, G. Yan, Y. Zhuang, J. Colloid Interface Sci. 381 (2012) 59.
- [13] X.L. Lin, L. Wu, Y.B. Liu, A.L. Ong, S.D. Poynton, J.R. Varcoe, J. Power Sources 217 (2012) 373–380.
- [14] D. Stoica, L. Ogier, L. Akrou, F. Alloin, J.-F. Fauvarque, Electrochim. Acta 53 (2007) 1596–1603.
- [15] L. Wu, T. Xu, D. Wu, X. Zheng, J. Membr. Sci. 310 (2008) 577–585.

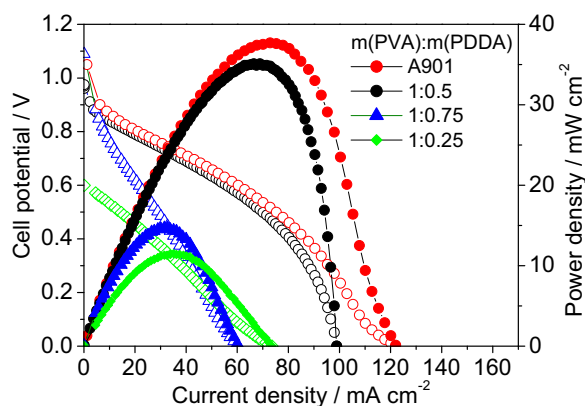


Fig. 9. Fuel cell performances of PVA/PDPA- OH^- alkaline membranes at room temperature and those compared with A901. The catalyst loading is 0.5 mg (Pt) cm⁻² both on the anode and cathode.

- [16] H. Herman, R.C.T. Slade, J.R. Varcoe, J. Membr. Sci. 218 (2003) 147–163.
- [17] Y. Wang, L. Li, L. Hu, L. Zhuang, J. Lu, B. Xu, Electrochem. Commun. 5 (2003) 662–666.
- [18] E. Komkova, D. Stamatialis, H. Strathmann, M. Wessling, J. Membr. Sci. 244 (2004) 25–34.
- [19] J.M. Yang, H.Z. Wang, C.C. Yang, J. Membr. Sci. 322 (2008) 74–80.
- [20] J.-S. Park, J.-W. Park, E. Ruckenstein, J. Appl. Polym. Sci. 80 (2001) 1825–1834.
- [21] L. Lebrun, N. Follain, M. Metayer, Electrochim. Acta 50 (2004) 985–993.
- [22] J.L. Qiao, J. Fu, L.L. Liu, Y.Y. Liu, J.W. Sheng, Int. J. Hydrogen Energy 37 (2012) 4580–4589.
- [23] A. Svang-Ariyaskul, R.Y.M. Huang, P.L. Douglas, R. Pal, X. Feng, P. Chen, L. Liu, J. Membr. Sci. 280 (2006) 815–823.
- [24] J.L. Qiao, T. Hamaya, T. Okada, Chem. Mater. 17 (2005) 2413–2421.
- [25] J.L. Qiao, T. Hamaya, T. Okada, J. Mater. Chem. 15 (2005) 4414–4423.
- [26] G. Merle, M. Wessling, K. Nijmeijer, J. Membr. Sci. 377 (2011) 1–35.
- [27] I. Kruusenberg, L. Matisen, Q. Shah, A.M. Kannan, K. Tammeveski, Int. J. Hydrogen Energy 37 (2012) 4406–4412.
- [28] B. Kowalewska, P.J. Kulesza, Electroanalysis 24 (2012) 254–263.
- [29] J.L. Qiao, J. Fu, L. Liu, J. Zhang, J. Xie, G. Li, Solid State Ionics 214 (2012) 6–12.
- [30] T.C. Zhou, J. Zhang, J.L. Qiao, L.L. Liu, G.P. Jiang, J. Zhang, Y. Liu, J. Power Sources 227 (2013) 291–299.
- [31] J.L. Qiao, T. Hamaya, T. Okada, Polymer 46 (2005) 10809–10816.
- [32] Y. Wu, C. Wu, J.R. Varcoe, S.D. Poynton, T. Xu, Y. Fu, J. Power Sources 195 (2010) 3069–3076.
- [33] J.L. Qiao, N. Yoshimoto, M. Morita, J. Power Sources 105 (2012) 45–51.
- [34] Q. Zhang, Q. Zhang, J. Wang, S. Zhang, S. Li, Polymer 51 (2010) 5407–5416.
- [35] M.R. Hibbs, C.H. Fujimoto, C.J. Cornelius, Macromolecules 42 (2009) 8316–8321.
- [36] J.F. Zhou, M. Unlu, J.A. Vega, P.A. Kohl, J. Power Sources 190 (2009) 285–292.
- [37] Z.J. Xia, Y.N. Sen, G.P. Jiang, X.X. Guo, J.H. Fang, L.L. Liu, J.L. Qiao, J. Yin, J. Membr. Sci. 390 (2012) 152–159.
- [38] I. Ran, L. Wu, J.R. Varcoe, A.L. Ong, S.D. Poynton, T.W. Xu, J. Membr. Sci. 415 (2012) 242–249.